

THERMAL CONVERSIONS OF CONJUGATED CYCLIC POLYENES WITH ENDOCYCLIC *TRANS* CARBON CARBON DOUBLE BONDS

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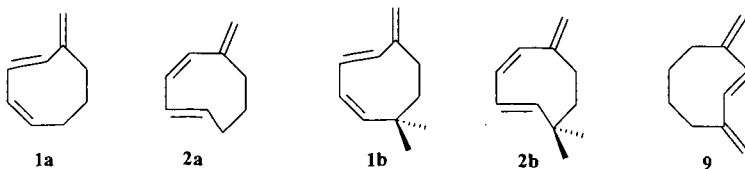
ABSTRACT

The strained monocyclic triene hydrocarbons (1*Z*, 3*E*)-5-methylene-1,3-cyclooctadiene (**1**) and (1*E*, 3*Z*)-5-methylene-1,3-cyclooctadiene (**2**) with endocyclic *trans* carbon carbon double bonds have been found to be key reactive intermediates in the complex thermal rearrangements of the *cis*-bridged bicyclic cyclobutene, 2-methylenebicyclo[4.2.0]oct-7-ene (**3**). Gasphase thermolysis (>160 °C) of **3** leads to three monocyclic trienes, **4**, **5** and **6**, and to two tricyclic alkenes, **7** and **8**. Indirect evidence for the involvement of **1** and **2** in the rearrangements of **3** follows from trapping intermediate **2** with furan and from their thermal generation by the cycloreversions of their independently synthesized *Diels-Alder* adducts with furan, respectively. Independent syntheses of the thermo-labile trienes **1** and **2** and of related hydrocarbons allows to directly investigate their thermal properties. Competing routes for stabilization of **1** - **3** to mono-, bi- and/or tricyclic products and their mechanistic implications are discussed. From experimental enthalpies of activation and molecular mechanics calculations energy profiles are modeled. Torquoselectivity as a function of ring size is discussed for *cis*-3,4-bridged cyclobutenes related to **3**.

I. INTRODUCTION

Thermal reorganizations of organic compounds often turn out to be highly stereoselective or even stereospecific. Frequently these reactions can be classified as concerted. These transformations usually demand only 'low' temperatures at which alternative reaction channels, e.g. those involving radical paths, are not accessible for energetic reasons. On the other side 'high' temperatures are required for reactions involving the thermal generation of radicals by breaking a carbon carbon bond. The cleavage of a simple C-C single bond necessitates an energy of about 80 - 90 kcal/mol, in crack processes of alkanes in many cases this is in accordance with temperatures up to 500 °C. However, temperatures for bond breaking can be lowered considerably by taking recourse to molecular strain and / or electronic stabilization of the carbon radical centers generated. This can be achieved to an extent that competition between concerted and multistep radical reactions has to be taken into account.

In this context monocyclic cyclobutenes easily undergo thermal cycloreversions to acyclic 1,3-butadienes in concerted reactions.¹⁻³ These archetypal electrocyclic reactions stereospecifically follow 'allowed' conrotation.^{1, 2} In simple cases the 'disallowed' disrotatory alternative is found to be energetically disfavored by about 10 kcal/mol.⁴ The profound electronic impact of substituents on the direction of conrotation observed in cyclobutene - butadiene reorganizations has found much attention, recently, from theory⁵ as well as from experiment.⁶⁻⁸ However, the stereochemical course of the cycloreversion of 3,4-bridged cyclobutenes which were structurally constrained proved to be considerably more complex. As a function of ring size of the annulated rings these compounds were found to thermally undergo 'allowed' conrotatory and / or 'forbidden' disrotatory ring openings to give *E/Z*-cyclooctadienes and / or *Z/Z*-stereoisomers.⁹⁻¹¹ The border-line case between both directions of cycloreversion, however, seems to rest with bicyclic cyclobutenes having attached a five or six membered ring.



Of special interest in this respect, therefore, is the thermal behavior of *cis*-3,4-bridged bicyclic cyclobutenes, e.g. 2-methylenebicyclo[4.2.0]oct-7-ene (**3**). The exocyclic methylene substituent in the 2-position of **3** should exert special effects on the mechanistic course and the energetics of the transformations of this hydrocarbon. Accessibility and thermal stability of the strained monocyclic conjugated triene hydrocarbons (1*Z*, 3*E*)-5-methylene-1,3-cyclooctadiene (**1**) and (1*E*, 3*Z*)-5-methylene-1,3-cyclooctadiene (**2**), expected to be central, although labile intermediates in the thermal rearrangements of **3**, are of key importance. We now report on independent syntheses of **1** and **2**. The thermal properties of these hydrocarbons have been determined as well as those of **3**. The results provide insight into the competing pathways of stabilization, as for instance by electrocyclization, by intramolecular cycloaddition, by direct geometric isomerization via diradicals, and / or by hydrogen migration. Suitably geminal methylated derivatives, **1b** and **2b**, and *E*-dimethylenecyclooctene **9**, significant for the question of a direct geometric stereomutation, have been included in our investigations. Energy profiles for the thermal reorganizations involved are modeled from experimental enthalpies of activation and molecular mechanics calculations. Torquoselectivity⁵ as a function of ring size is discussed for *cis*-3,4-bridged cyclobutene **3** and related compounds.

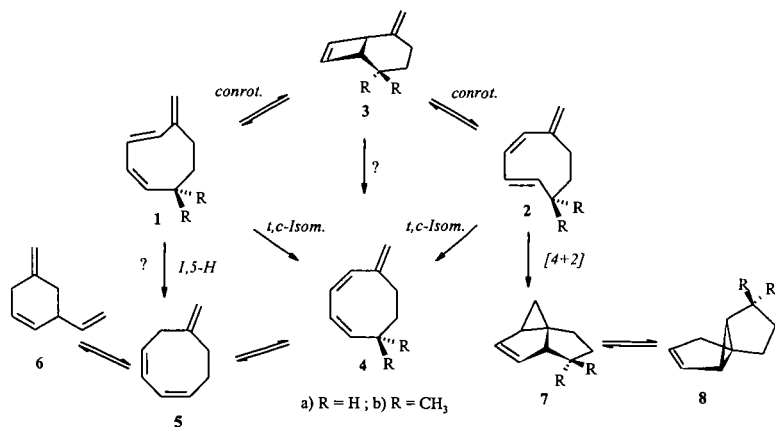
II. PROCEDURE

Thermolyses of **3** have been performed at low pressure (1-5 mbar) in the gasphase in a conditioned 20 l pyrex vessel. The flask was heated in an air-thermostat with a temperature constancy better than 0.1 °C and was connected to a high vacuum line with greaseless stopcocks. Kinetic measurements have been followed gaschromatographically. Rearrangements of the thermally labile hydrocarbons **1**, **2** and **9** had to be carried out in solution. Toluene-*d*₈ and cyclohexane-*d*₁₂ were used as solvents to follow the reactions quantitatively by ¹H-NMR spectroscopy at 400 MHz.

Experimental details of the synthetic procedures for the relevant compounds will be reported elsewhere.

Molecular mechanics calculations have been performed with the programs MM2ERW¹² and MMEVBH¹³ developed by W. R. Roth¹⁴ and co-workers on the basis of Allinger's¹⁵ MM2 procedure. The MM2ERW¹² forcefield allows one to calculate conjugated π -systems with high accuracy without embarking on quantum-mechanical methods. The MMEVBH procedure has been developed^{13,14} to calculate heats of formation of hydrocarbons, conjugated and non conjugated polyenes as well as those of radicals and diradicals.

Scheme 1. Mechanistic Pathways for the Thermal Reorganizations of C₉H₁₂ Isomers **1** - **3**, and Geminal Dimethyl Substituted Derivatives.



III. RESULTS

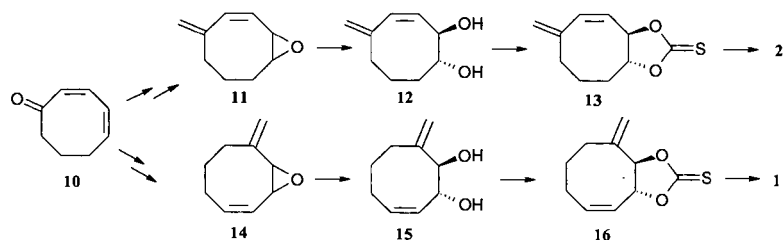
In the temperature range of about 165 to 215 °C gasphase thermolysis of the bridged bicyclic vinylcyclobutene **3** results in the formation of five new isomeric hydrocarbons. These can be grouped into two sets, on the one side into the three monocyclic trienes **4**, **5**, and **6**, and on the

other side into two tricyclic alkenes **7** and **8**, with **4** and **7** constituting the main products.¹⁶ The kinetics of the decrease of **3** follows a first order reaction with $\log A = 13.27 \pm 0.06$ and $E_a = 36.13 \pm 0.12$ kcal/mol. However, not all of the products are primary ones. Under the reaction conditions conjugated triene **4** is in fast equilibrium with its 1,5-hydrogen shift product **5**. From this, secondarily the monocyclic unconjugated **6** is formed. The activation parameters for the mutual conversions $4 \leftrightarrow 5 \leftrightarrow 6$ have been determined independently at lower temperatures by starting with **5**.¹⁷ The tricyclic alkene **7** slowly undergoes a *vinylcyclopropane-cyclopentene* rearrangement to spiroalkene **8**. In view of our experimental findings and earlier results on *cis*-bicyclo[4.2.0]oct-7-ene¹⁸ the mechanistic pathways given in Scheme 1 have to be taken into account.

Central to product formation from **3** are the properties of the strained trienes **1** and **2** which could be formed by allowed conrotatory cycloreversion with inward and outward rotation of the exocyclic methylene substituent. However, these *trans*-cycloalkenes are unstable at the high temperatures necessary to convert **3**. Indirect evidence for the involvement of **1** and **2** is derived from our findings that **2**, but not **1**, can be trapped in the presence of furan as *trans*-[4+2] cycloaddition products and that thermal decomposition ($T > 155^\circ\text{C}$) of the four *Diels-Alder* adducts possible from **1** and **2** with furan, which all have been synthesized independently, results in the same product mixtures as that found from **3**.¹⁶ Mechanistically still unanswered are the questions if the observed *Z,Z*-product **4** is generated from **3** by direct disrotation, by direct cleavage of a double bond $1 \rightarrow 4$ or $2 \rightarrow 4$, respectively, or if a multistep sequence $3 \rightarrow 1 \rightarrow 5 \rightarrow 4$ is followed with a 1,5-hydrogen shift in **1** as the crucial step.

Substituting hydrogen by geminal methyl groups as in **3b** after electrocycloization should lead to labile triene intermediates **1b** and **2b**. In **1b** stabilization by a concerted 1,5-hydrogen shift would be blocked and recycloization should dominate. Results of gasphase thermolyses at $175 - 220^\circ\text{C}$ with **3b** as an educt show, indeed, **7b** to be the main product followed by rearrangement to **8b**. The *Z,Z*-triene **4b** is formed only to a minor extent.¹⁹

Scheme 2. Synthetic Routes to Trienes (1*Z*, 3*E*)-5-methylene-1,3-cyclooctadiene (**1**) and (1*E*, 3*Z*)-5-methylene-1,3-cyclooctadiene (**2**).



Independent syntheses of the central intermediates **1** and **2** are accomplished for the first time by following a modified Corey/Winter²¹ protocol as shown in Scheme 2. Using such a sequence for the synthesis of strained trienes seems to be without precedent. Key steps are stereospecific ring openings of the vinyloxiranes **11** and **14** to give *trans*-diols **12** and **15**, respectively, after regioselective formation from dienone **10**, and desulfuration of the *trans*-thionocarbonates **13** and **16** at about room temperature and at low pressures to generate **1** and **2** with high isomeric purity.²⁰ The structures of both isomers have been characterized without doubt by NMR spectroscopy. Additionally, the *E*-configuration of the central carbon carbon double bond in **1** has been secured by formation of the same *Diels-Alder* adducts with furan as those known from an independent route¹⁶ and by X-ray structure analysis of one of the adducts with diphenylisobenzofuran.²⁰ Synthesis of the geminal methylated isomers **1b** and **2b** proved to be more difficult and a modified route using β -hydroxyphosphinioxides as intermediates had to be taken.²² *E*-Dimethylenecyclooctene **9** is obtained by a multistep sequence to the *Z*-isomer followed by sensitized photoisomerization.

Slightly above room temperature triene **1** with a central *trans* double bond starts to cyclorevert to **3** and to isomerize to *Z,Z*-triene **4** in a 2 : 1 ratio, approximately. Not completely conjugated triene **5**, stable at the reaction conditions, is not observed. In toluene-d₈ and followed at temperatures of $30 - 70^\circ\text{C}$ reaction $1 \rightarrow 3$ shows $\log A/s^{-1} = 13.2 \pm 0.2$ and $E_a = 25.6 \pm 0.3$ kcal/mol. Trienes **2** and **2b** with the *trans* double bond in the end of the conjugated system prove

to be thermally more stable. At 60 -120 °C they predominantly undergo electrocyclization to **3** and **3b** with $E_a = 26.7 \pm 0.3$ kcal/mol and $E_a = 26.9 \pm 0.9$ kcal/mol, respectively. The *Z,Z*-trienes **4** are formed, but to a smaller extent; from **2b** traces of **7b** are observed. However, thermolyses of **2** and **2b** are complicated by some dimerization. At 50 - 95 °C *E*-cyclooctene **9** isomerizes to the *Z*-isomer with $E_a = 25.8$ kcal/mol, exclusively.²⁰

Schematic energy profiles of the reactions involved can be modeled by combining our experimentally determined activation parameters with enthalpies of formation calculated by the above forcefield programs for educts, products and the reactive intermediates participating. It is clearly shown that besides dominant electrocyclization in the first two cases the reactive trienes **1**, **2** and **9** can be stabilized competitively by direct double bond cleavage to diradical transition structures followed by rotation and recombination to their thermally more stable *Z*-isomers, even at temperatures close to room temperature. Ring opening in **3** by disrotation and stabilization of *trans*-triene **1** by a 1,5-hydrogen shift does not take place. These findings are discussed with those of our earlier results on thermal rearrangements of hydrocarbons related to **3** which have contracted rings^{23, 24} and those of the relevant literature.

In addition, it is shown that by using substrates **3** stereospecifically substituted at the *exocyclic* methylene carbon the formations of the tricyclic products **7**, formally intramolecular *Diels-Alder* reaction products, follow multistep routes via diradical intermediates.^{16, 19} Nevertheless, in some cases product formation with high stereoselectivity has been found.

IV. CONCLUSIONS

Highly strained monocyclic *trans*-trienes (1*Z*, 3*E*)-5-methylene-1,3-cyclooctadiene (**1**) and (1*E*, 3*Z*)-5-methylene-1,3-cyclooctadiene (**2**), obtained by direct syntheses for the first time, are established as key intermediates in the multiple thermal rearrangements of the 3,4-bridged vinylcyclobutene 2-methylenebicyclo[4.2.0]oct-7-ene (**3**). **1** and **2** stabilize competitively by electrocyclization to **3** and to their less strained *Z*-isomers **4** by direct double bond cleavage even at temperatures slightly above room temperature. The latter also applies to the thermal stabilization of *E*-dimethylenecyclooctene **9**. Ring opening in **3** by disrotation and by 1,5-hydrogen shift in **1** are not important.

Combining experimental enthalpies of activation and the results of forcefield calculations the energy profiles of these hydrocarbon reactions show that diradical transition structures are accessible and are of major importance. These findings are also of relevance to other hydrocarbon systems comprising 3,4-bridged cyclobutene structures.

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